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Single-Wall Carbon Nanotubes Synthesis by Means of UV Laser Vaporization: Effects of the Furnace Temperature and the Laser Intensity Processing Parameters

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ABSTRACT

Carbon single-wall nanotubes (SWNTs) have been successfully synthesized by means of KrF laser vaporization of a Co-Ni-doped graphite pellet in a flowing argon atmosphere. The effects of two key processing parameters, namely the furnace temperature (in the 25-1150 °C range) and the laser intensity (in the $0.8\text{--}4.4 \times 10^8 \text{ W/cm}^2$ range), on the yield and the structural characteristics of the carbon SWNTs were investigated. By characterizing the obtained deposits by means of transmission electron microscopy and micro-Raman spectroscopy techniques, we were able to identify a threshold temperature as low as $\sim 550^\circ\text{C}$, below which no carbon SWNTs can be grown. The increase of the furnace temperature from 550 to 1150 °C was found to lead not only to a significant increase in the SWNTs yield but also to the formation of larger SWNTs bundles. Raman analysis have also revealed that the diameter distribution peak shifts from ~ 1.05 to $\sim 1.22 \text{ nm}$ as the temperature is raised from 550 to 1150 °C. At the highest furnace temperature of 1150 °C, we also found that a minimum laser intensity of about $1.6 \times 10^8 \text{ W/cm}^2$ is required to grow carbon SWNTs by means of the KrF laser. Higher laser intensities have resulted in a higher yield of SWNTs with relatively thicker bundles. Moreover, the increase of the laser intensity was found to promote the growth of 1.22 nm-diameter nanotubes to the detriment of thinner carbon nanotubes (1.05 and 1.13 nm-diameters).

INTRODUCTION

Since the first demonstration in 1995 of the use of a Q-switch Nd:YAG laser as a new alternative to synthesize single-wall carbon nanotubes [1], the field of laser synthesis of carbon nanotubes continues to attract great interest for either fundamental or applications purposes. Indeed, the laser vaporization technique stands out by its capacity to produce exclusively single-wall nanotubes (SWNTs) at the highest yield ever reported ($\sim 80\%$) [2]. Focus has been put on the study of the effect of many processing parameters in order to optimize the technique. For example, the influence of the furnace temperature was investigated for dual pulse Nd:YAG laser [3] and pulsed CO₂ laser [4] to conclude that a higher furnace temperature leads not only to the production of a higher fraction of SWNTs (against other carbonaceous species) but also to a preferential growth of SWNTs of larger diameters. Other studies have reported on the influence of laser intensity for single and/or dual pulse Nd:YAG laser and established the existence of an optimal laser intensity at which SWNTs are preferentially grown [5, 6]. On the other hand, all the research reported to date on the laser synthesis of SWNTs was carried out using lasers emitting in the visible and/or infrared (from 532 nm to 10.6 μm) part of the spectrum. The growth of carbon nanotubes by using lasers emitting in the UV domain remains unexplored.

In this paper, we report on the successful synthesis of SWNTs by means of UV laser vaporization. We will focus here on the study of the influence of two processing parameters, namely the furnace temperature and the laser intensity, on the growth of SWNTs. In particular, it is found that carbon SWNTs can be grown by means of KrF laser vaporization at a temperature (550 °C) lower than the lowest temperature (850 °C) required when using Nd:YAG lasers.

EXPERIMENTAL

Carbon SWNTs were produced by ablating a Co-Ni-doped graphite pellet by means of a pulsed KrF excimer laser (wavelength = 248 nm; pulse duration = 15 ns; repetition rate = 30 Hz). The target was fabricated by pressing a mixture of a graphite powder (-325 mesh), a carbon cement and Co-Ni powder catalyst (0.6% at.) at a pressure of 5 kPsi. The obtained pellet is cured at 800°C for 8h, heated at 1150 °C for 12h in a flowing argon atmosphere and then placed in a quartz tube in the center of the furnace. During synthesis, the laser beam was rastered over the target surface in order to ensure a uniform ablation. KrF laser vaporization was carried out in a flowing argon atmosphere (300 SCCM, 500 Torr) at different furnace temperatures ranging from room temperature (RT) to 1150 °C and with various on-target laser intensities in the $(0.8\text{--}4.4) \times 10^8 \text{ W/cm}^2$ range. The laser vaporized species were carried by the flowing argon gas towards a water-cooled copper collector, located at the exit end of the furnace, on which the nanotubes were collected.

The as-produced carbon deposits (no purification processing was used) were systematically characterized as a function of the processing parameters by means of: (i) transmission electron microscopy (TEM) (FEG Philips CM20 microscope, acceleration voltage of 200kV), (ii) high-resolution TEM (HRTEM) imaging (Gatan image filter multiscan camera) and (iii) micro-Raman spectroscopy (Renishaw Imaging Microscope Wire^{PM}, argon ion excitation with $\lambda_{\text{exc}} = 514.5 \text{ nm}$).

RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of the samples produced at various furnace temperatures ranging from RT to 1150°C with a KrF laser intensity of $3.5 \times 10^8 \text{ W/cm}^2$. The Raman peaks in the low frequency region ($100\text{--}300 \text{ cm}^{-1}$) are due to the radial breathing modes (RBM) of the nanotubes, and their position (ω in cm^{-1}) can be directly related to the nanotube diameter (d in nm) by using the relation ($d = 223.75/\omega$) proposed by Bandow *et al.* [3]. For furnace temperatures < 550 °C, the absence of RBM peaks in the low-frequency part of the Raman spectra clearly indicates that no nanotubes were formed at these low temperatures. In contrast, the strong scattering RBM peaks observed for temperatures $\geq 550 \text{ °C}$ are a typical signature of SWNT containing samples. Indeed, the main peaks (centered around 183, 198 and 213 cm^{-1}) that compose the RBM band are due to carbon SWNTs having diameters of 1.22, 1.13 and 1.05 nm, respectively. As the furnace temperature is raised from 550 to 1150 °C, the RBM peak assigned to the 1.22 nm nanotubes becomes more intense to the detriment of the 1.05 and 1.13 nm-diameter nanotubes. This shift of the maximum of the nanotube diameter distribution (from 1.05 to 1.22 nm) suggests that the furnace temperature increase favors the growth of thicker nanotubes. The increase of the nanotube diameter with the growth temperature has been also observed for SWNTs produced by means of dual pulse Nd:YAG laser configuration [3].

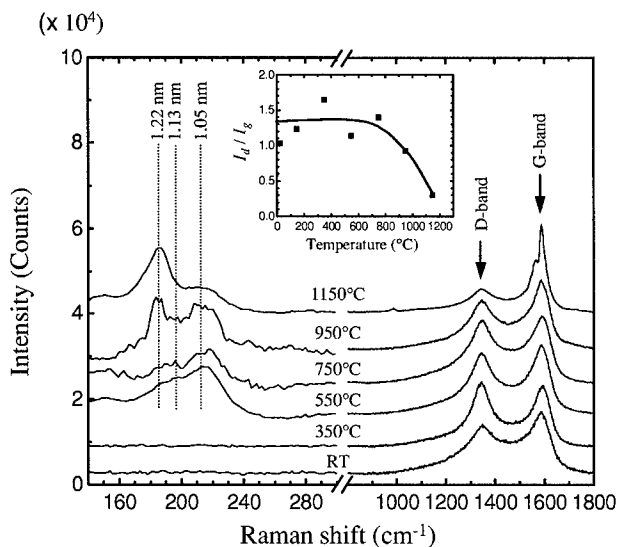


Figure 1. Raman spectra of the UV laser produced deposits at various furnace temperatures ranging from RT to 1150 °C. The RBM Raman peaks are identified (dashed vertical lines) along with their corresponding carbon SWNT diameters in nm. The inset shows the variation of the I_d/I_g ratio of the deposits as a function of the furnace temperature.

The high-frequency G and D Raman bands are due to the graphitic E_{2g} tangential acoustic mode of the SWNTs and to disordered sp^2 carbon, respectively [7]. The ratio of the intensities of the D-band to the G-band (I_d/I_g) is proportional to the relative amount of amorphous carbon or other disordered sp^2 carbon species [7]. The inset of figure 1 shows that the I_d/I_g ratio oscillates around an average value of $\sim 1.3 \pm 0.3$ for furnace temperatures ≤ 750 °C, and then steadily decreases for higher temperatures to reach a value of ~ 0.3 at 1150 °C. This indicates that high processing temperatures lead to a lower fraction of disordered carbon in the deposits. The resonant enhancement of the G-band (which is a consequence of the high yield of SWNTs observed at high temperatures) may also contribute to the observed lowering of the I_d/I_g ratio.

Figure 2 shows the typical TEM micrographs of the deposits at selected furnaces temperatures. At a furnace temperature of 350 °C, an extensive search failed to uncover any SWNT in the deposit (this is consistent with the absence of the RBM band in the corresponding Raman spectrum). The carbon soot was rather composed of graphitic cages having a concentric layer morphology and an average diameter in the 5-10 nm range (inset of Fig. 2a). At a temperature of 550 °C, bundles of SWNTs having diameters ranging from 10 to 15 nm were found in low yield. Figure 2b is a typical TEM image of the deposits synthesized at 550 °C where a loop-like bundle having 14 nm in diameter and ~ 1.4 μm in length is clearly observed (The HRTEM micrograph shown in the inset of Fig. 2b confirms the typical internal structure of a SWNT bundle). In addition to the nanotubes, the carbon nanostructures that compose also the deposit at 550°C were found to consist of interconnected fullerene-like structures [8]. When the furnace temperature is raised to 1150°C, the deposit was found to contain a significantly higher fraction of SWNTs (Fig. 2c) self-organized in larger bundles (15-20 nm-diameter). Moreover, the average diameter of the SWNTs was found to be 1.2 ± 0.3 nm, as deduced from HRTEM micrographs using direct lattice images of nanotubes bundles lying parallel to the microscope focal plane [2]. At 1150°C, the carbon nanoparticles co-produced with the SWNTs were found

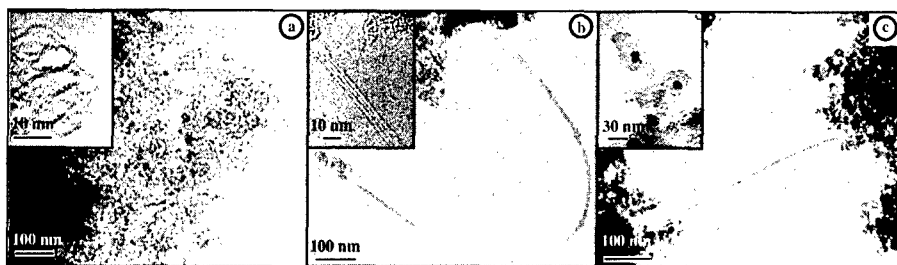


Figure 2. TEM micrographs of the deposits grown at (a) 350 °C, (b) 550 °C and (c) 1150 °C furnace temperatures.

to have a diameter in the 30-50 nm range and were most often constituted of amorphous carbon surrounding catalyst nanoclusters (see inset of Fig. 2c).

At the highest furnace temperature of 1150 °C, the effect of the laser intensity on the growth of SWNTs was investigated over the $0.8\text{--}4.4 \times 10^8 \text{ W/cm}^2$ range. A laser intensity of $1.6 \times 10^8 \text{ W/cm}^2$ was identified as the lowest value that produces sufficient amount of SWNTs containing soot that permits subsequent characterizations. Figure 3 displays the Raman spectra of the SWNT samples produced at increasing laser intensities. The RBM band clearly indicates the presence of carbon nanotubes having diameters in the (1.05- 1.50) nm range. One can note that as the laser intensity is increased, the 1.22 nm-diameter peak becomes sharper and more intense to the detriment of the other components. A tendency to favor the formation of nanotubes with larger diameters as the laser intensity is increased have been also reported when Nd:YAG lasers were used [6,9].

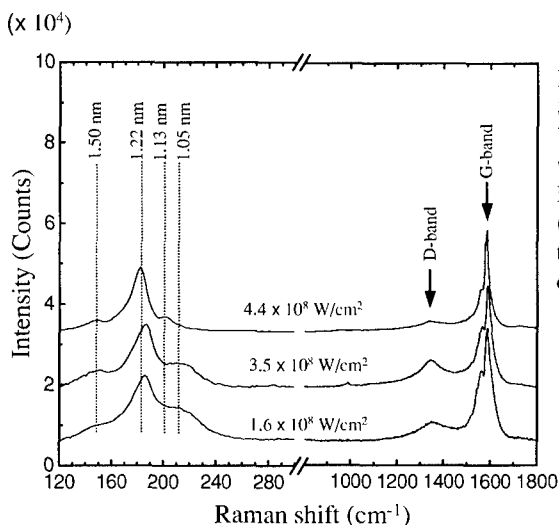


Figure 3. Raman spectra of the SWNTs synthesized by means of UV laser vaporization at 1150 °C with various laser intensities. The RBM Raman peaks are identified (dashed vertical lines) along with their corresponding carbon SWNT diameters in nm.

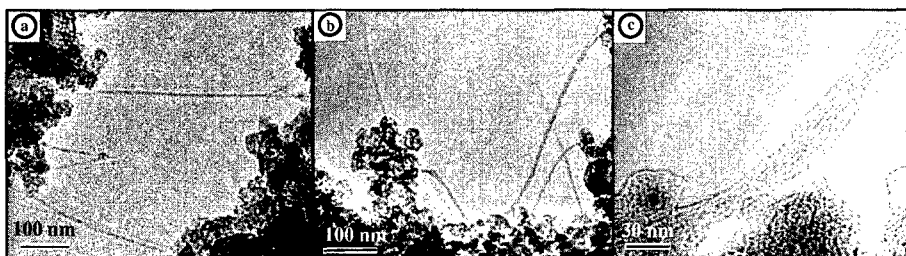


Figure 4. TEM micrographs of SWNT samples produced at 1150 °C with various KrF laser intensities: (a) $2.7 \times 10^8 \text{ W/cm}^2$, (b) $3.5 \times 10^8 \text{ W/cm}^2$ and (c) $4.4 \times 10^8 \text{ W/cm}^2$.

Figure 4 shows TEM micrographs taken from SWNT samples produced at different laser intensities. At low laser intensities ($1.6\text{--}2.7 \times 10^8 \text{ W/cm}^2$), the deposit is constituted of SWNT bundles having an average diameter of 12 nm along with catalyst nanoclusters embedded within a-carbon nanoparticles (30-50 nm-diameter). The morphology and the diameter of these particles were found to remain insensitive to the laser intensity over all the investigated range. However, the fraction of nanotubes in the deposits was found to increase as the laser intensity is raised to 3.5 and $4.4 \times 10^8 \text{ W/cm}^2$. The diameter of the SWNT bundles also increases with the laser intensity. SWNT bundles having a diameter of up to ~ 30 nm were observed at the highest laser intensity investigated here (see Fig. 4c).

CONCLUSION

The synthesis of single-wall carbon nanotubes by means of KrF laser vaporization is demonstrated. It is shown that SWNTs can be grown at a temperature as low as 550 °C. At a furnace temperature of 1150 °C, it is found that a minimum laser intensity of about $1.6 \times 10^8 \text{ W/cm}^2$ is required to produce carbon SWNTs. The obtained results show that the increase of the furnace temperature leads to a higher yield of SWNTs and favors the growth of larger SWNTs organized in thicker bundles. Similar effects, but at a lesser degree, were also observed with the increase of the laser intensity. Such a similarity could be explained by considering that an increase of the laser intensity would lead to an enhancement of the temperature of the surface target during laser vaporization. Indeed, for the relatively low laser intensities investigated here, a major part of the laser energy is expected to be absorbed at the target near-surface, acting thereby as a local furnace. Finally, the extension of the useful laser wavelengths to the UV domain not only offers a new alternative to produce efficiently SWNTs, but might also open new prospects in the fundamental and/or application aspects of laser synthesized nanotubes.

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